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Alkylation on Synthetic Zeolites

III. Alkylation of Toluene with Methanol and Formaldehyde on Alkali Cation Exchanged Zeolites

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Alkylation of toluene with methanol and with formaldehyde was studied over the alkali cation exchanged zeolites. It was found that xylenes were formed by alkylation of the benzene ring of toluene on Li exchanged zeolites. However, a mixture of styrene and ethylbenzene was formed by the alkylation of the methyl group of toluene on Na, K, Rb and Cs exchanged zeolites, and each alkylation proceeded very selectively. Formaldehyde was more reactive than methanol in both alkylations, but gave similar aromatic products to that of methanol. Under the optimum conditions in the alkylation with formaldehyde, the yields of styrene and ethylbenzene were 10.3 and 2.6% on RbX catalyst, respectively, and the yield of xylenes was 10.7% on LiY catalyst.

The yield of the alkylation products of the benzene ring of toluene was related to the weak acidity of Li zeolites, and was depressed by a basic reagent. On the other hand, the yield of the alkylation products of the methyl group of toluene was depressed by an acidic reagent, and was not poisoned by aniline. Further, it was detected that K and Rb zeolites have solid basicity. It is therefore suggested that the formation of xylene and that of both styrene and ethylbenzene depends on the catalyst acidity and basicity, respectively.

INTRODUCTION

It is known that the alkali cation exchanged zeolites have little activity to promote any reactions proceeding through a carbonium ion form. However, it has been found that the alkali exchanged zeolites have appreciable catalytic activity in dehydration of alcohols (*1*, *2*), methylmigration of anisole (*3*), dealkylation of cumene (*4*) and the reaction of acetic anhydride with hydrogen sulfide (*5*). It is also reported that Li exchanged zeolite always has the most catalytic activity among the alkali metal cations in the above-mentioned reactions. It has also been reported that the isomerization of *n*-butenes on NaX proceeds through a radical form (*6*).

We have reported that the alkylation of toluene with methanol on NH_4^+, di- and trivalent cation exchanged zeolites produced a xylene mixture which was rich in *p*-isomer (*7*, *8*), and observed that no alkylation reaction occurred on alkali cation exchanged zeolites except LiY at the same reaction temperature range (< 250°C). At a higher temperature, however, it was found that toluene was alkylated with methanol and with formaldehyde on the alkali cation exchanged zeolites, and converted selectively to xylenes or to a mixture of styrene and ethylbenzene according to the kind of exchanged cations. Sidorenko *et al.* (*9*) have reported that the alkylation of toluene with methanol proceeds on alkali cation exchanged zeolites, producing a mixture of xylenes, styrene and ethylbenzene. They proposed a reaction scheme in which styrene was produced by the alkylation of toluene with formaldehyde formed by dehydrogenation of methanol, and a part of the styrene was hydrogenated to ethylbenzene. Then, we studied in detail the alkylation of toluene with methanol and with formaldehyde on various alkali cation exchanged X and Y zeolites, to examine the correlation between the selective formation of alkylates and the catalyst properties.

EXPERIMENTAL METHODS

Material

Toluene and methanol, having a purity of over 99%, were obtained from a commercial source. An aqueous solution of formaldehyde was prepared from paraformaldehyde dissolved in boiling water. The formaldehyde content was determined by the sodium sulfite method *(10)*.

Catalyst

Alkali cation exchanged zeolites were prepared by a conventional cation exchange procedure using a 0.5–1 *N* aqueous solution of corresponding alkali acetate or chloride and Linde 13X(raw NaX) or SK-40(raw NaY), and the degree of cation exchange was measured by flame photometry. The exchanged zeolites were pelleted without a binder, crushed and sized in 8–14 mesh, and were calcined at 500°C for 3 hr before reaction.

Analysis

The reaction mixture was analyzed by gas chromatography using a 3 mm × 4 m stainless steel column with stationary phase Benton 34 and DNP on Celite 545. The carrier gas was H_2(0.6 kg/cm^2 input pressure) and the analysis temperature was 95°C.

Measurement of Catalyst Acidity by IR

All infrared measurements were made with adsorbents in the form of self-supporting wafers prepared by pressing 20 mg of fine powder in a 20 mm diameter die at 400 kg/cm^2. The wafers were electrically heated at 500°C for 1 hr while being evacuated in the infrared cell. After calcination, the wafers were exposed to pyridine vapor at 15 mm Hg pressure at 100°C for 30 min, and were evacuated at 200°C for 1 hr. Further, the pyridine-adsorbed wafers were exposed to water vapor at room temperature for 30 min and were then evacuated at 200°C for 1 hr. The spectra of the wafers were recorded at room temperature.

Apparatus and Procedure

Experiments were carried out in a fixed bed type apparatus with a continuous flow system at atmospheric pressure. The catalyst was placed in an electrically heated quartz reactor and, after the air was replaced with nitrogen, the catalyst was calcined at 500°C for 3 hr, and then brought to the reaction temperature *in situ*. Toluene and an aqueous solution of formaldehyde, or a mixture of toluene and methanol, were fed by microfeeders, and were carried by nitrogen to the catalyst bed. The product was cooled with an ice trap, and samples for analysis were collected periodically.

RESULTS AND DISCUSSION

In the alkylation of toluene with formaldehyde, the activity of the catalyst changed considerably with process time (Fig. 1). In the case of methanol, the catalyst activity changed gradually with

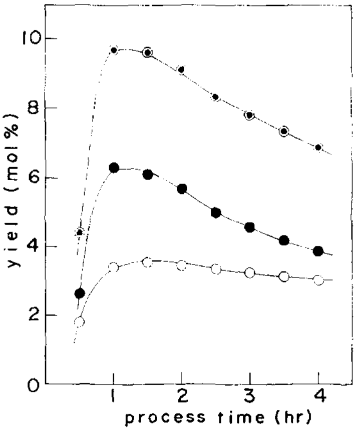

FIG. 1. Activity change with process time in the alkylation with formaldehyde. Conditions: W/F = 25 (g hr/mole), temp = 425°C, toluene/formaldehyde = 6, formaldehyde concn = 43 (wt %). Catalyst: KX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

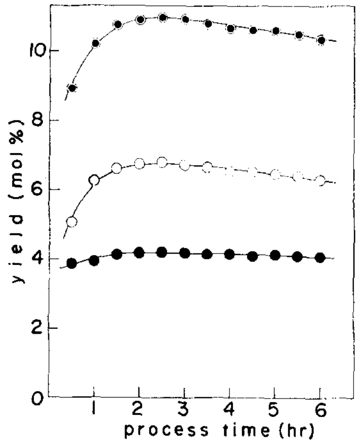

FIG. 2. Activity change with process time in the alkylation with methanol. Conditions: $W/F = 25$ (g hr/mole), temp = 425°C, toluene/methanol = 6. Catalyst: RbX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

process time (Fig. 2). These changes of the catalyst activity may be due to continuous deactivation of catalyst and to the parallel side-reaction of alkylating reagents. It was also observed that the yield of products by the side-reaction of alkylating reagents, that is dimethyl ether, CO, H_2 and CO_2, was very large at the initial stage of this process. Thus the data of the experiments were taken during the highest yield of aromatic products which usually occurred at 1 hr and 2 or 3 hr of process time in the case of formaldehyde and methanol, respectively. As the experiment was always carried out in excess of toluene, the yield of products was calculated as follows:

$$\text{yield} = \frac{\text{moles of products}}{\text{moles of fed methanol or formaldehyde}} \times 100 \text{ (mole \%)}$$

In most cases, over 90% of the fed methanol or formaldehyde was converted. Most of the alkylating reagents which were not converted to the alkylaromatics were consumed by producing dimethyl ether and cracking to CO, H_2 and CO_2. The effect of reaction conditions, which are reaction temperature, contact time and molar ratio of reactants, on the side-chain alkylation of toluene was studied using KX or RbX as a catalyst. Further, the activity of various catalysts in the alkylation of the side chain of toluene and in the alkylation of the benzene ring of toluene was discussed.

1. Reaction Conditions

As a carrier gas, 5 moles of nitrogen/mole of reactants were fed as described in previous papers (*7*, *8*). Above this molar ratio, there was no noticeable effect on the yield (Fig. 3).

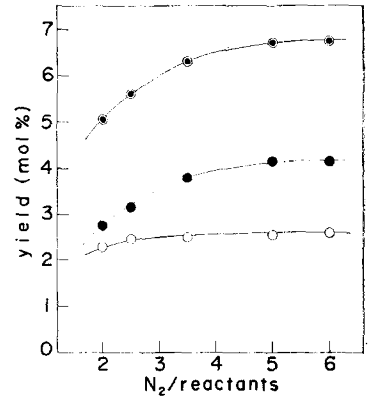

FIG. 3. Effect of carrier gas in the alkylation with formaldehyde. Conditions: $W/F = 25$ (g hr/mole), temp = 425°C, toluene/formaldehyde = 4.2, formaldehyde concn = 20 (wt %). Catalyst: KX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

Reaction temperature. Under constant contact time and ratio of reactants, the effects of reaction temperature on the alkylation of toluene with methanol and with formaldehyde on RbX and KX are shown in Figs. 4 and 5, respectively. In both cases, the optimum reaction temperature was 425°C. At a higher temperature than 425°C, decomposition of the alkylating reagents occurred rather than alkylation.

Contact time. As the indication of contact time, we used W/F, defined as follows:

$$W/F = \frac{\text{catalyst wt (g)}}{\text{feed rate of reactants (toluene + methanol or formaldehyde) (mole/hr)}}.$$

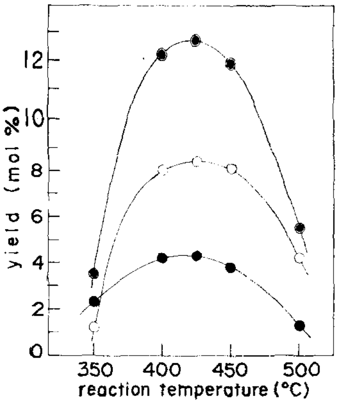

FIG. 4. Effect of reaction temperature in the alkylation with methanol. Conditions: $W/F = 50$ (g hr/mole), toluene/methanol = 3. Catalyst: RbX. (◉) total C_8 aromatics, (●) styrene; (○) ethylbenzene.

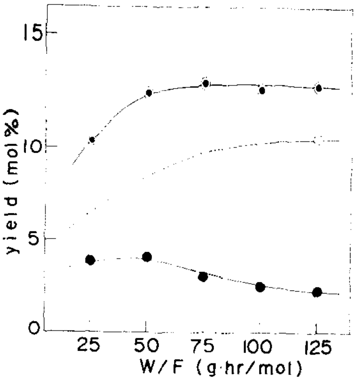

FIG. 6. Effect of contact time in the alkylation with methanol. Conditions: temp = 425°C, toluene/methanol = 3. Catalyst: RbX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

The results of alkylation with methanol and with formaldehyde on RbX and KX at 425°C with the variation of W/F are shown in Figs. 6 and 7, respectively. Total yields of C_8 aromatics did not change markedly in the case of methanol and formaldehyde with W/F of higher than 50 and 20, respectively. With higher contact time, however, the yield of styrene decreased while that of ethylbenzene increased. It was suggested that it would be possible to hydrogenate the produced styrene to ethylbenzene. Actually, when hydrogen was used as a carrier gas, the total yield of styrene and ethylbenzene was not markedly changed, but the yield of styrene was only one-tenth of that in a nitrogen carrier.

Molar ratio of reactants. The yields of C_8 aromatics were increased with the molar ratio of toluene to alkylating reagents (Figs. 8 and 9). Further, the effect of water on the alkylation was examined, since an aqueous solution was generally used as the formaldehyde source (Fig. 10). As shown in Fig. 10, the yield of products increased with the formaldehyde concentration. This increase of the yield cannot be expected if the water in this reaction had merely a role of diluent, like nitrogen (see Fig. 3). From these results, it was concluded that water poisoned this alkylation.

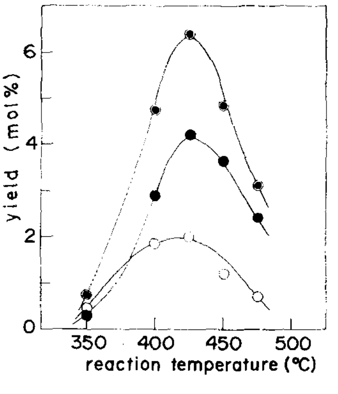

FIG. 5. Effect of reaction temperature in the alkylation with formaldehyde. Conditions: $W/F = 25$ (g hr/mole), toluene/formaldehyde = 4.2, formaldehyde concn = 20 (wt %). Catalyst: KX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

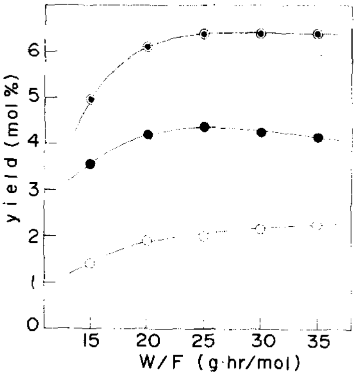

FIG. 7. Effect of contact time in the alkylation with formaldehyde. Conditions: temp = 425°C, toluene/formaldehyde = 4.2, formaldehyde concn = 20 (wt %). Catalyst: KX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

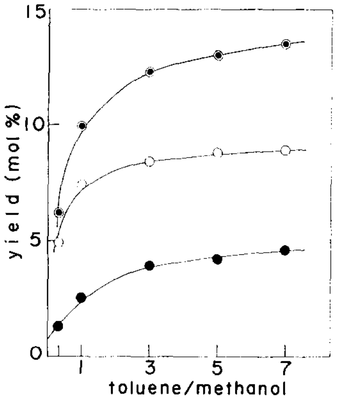

FIG. 8. Effect of molar ratio of reactants (toluene/methanol). Conditions: $W/F = 50$ (g hr/mole), temp = 425°C. Catalyst: RbX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

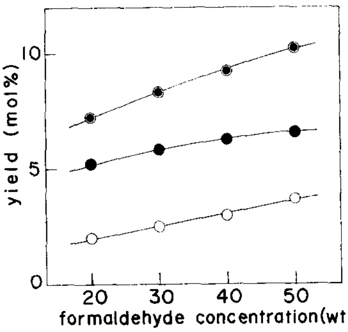

FIG. 10. Effect of formaldehyde concentration. Conditions: $W/F = 25$ (g hr/mole), temp = 425°C, toluene/formaldehyde = 6. Catalyst: KX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene.

However, an aqueous solution containing over 50 wt % formaldehyde was not stable, because paraformaldehyde was easily precipitated at room temperature.

2. *Catalyst Activity*

Catalyst activity of alkali zeolites. The results of alkylation of toluene with methanol and with formaldehyde on alkali exchanged zeolites are shown in Tables 1 and 2, respectively. In this alkylation, different alkylaromatics were produced on the different alkali cation exchanged zeolites. On Li exchanged zeolites, xylenes were only produced as C_8 aromatics by the selective alkylation of the benzene ring of toluene.

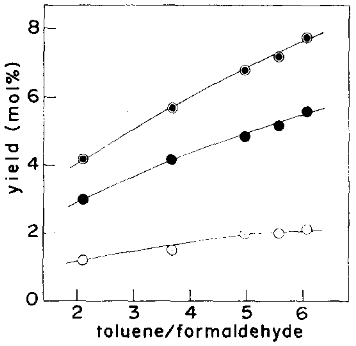

FIG. 9. Effect of molar ratio of reactants (toluene/formaldehyde). Conditions: $W/F = 25$ (g hr/mole), temp = 425°C, formaldehyde concn = 20 (wt %). Catalyst: KX. (◉) total C_8 aromatics; (●) styrene; (○) ethylbenzene

On Na, K, Rb and Cs exchanged zeolites, however, styrene and ethylbenzene were produced selectively without any xylene isomers by the alkylation of the methyl group of toluene. Only on 13X and SK-40 were mixture of xylenes, styrene and ethylbenzene produced. However, it was recently pointed out by Lombardo, Sill and Hall (*11*) that 13X and SK-40 contain small amounts of multivalent cations, and the catalytic activity of 13X and SK-40 was attributed to these cation impurities.

It is well known that the multivalent cation exchanged zeolites have acidic properties, and catalyze aromatic ring alkylations. Actually on NaX and NaY, which were prepared by the back-exchange of 13X and SK-40 with an aqueous solution of sodium acetate, styrene and ethylbenzene were produced without xylenes. This result showed that the formation of xylenes on 13X and SK-40 was due to the multivalent cation impurities. Thus, the aromatic products of this alkylation changed dramatically with the kind of exchanged alkali cation. On the other hand, the change of alkylating agents did not affect the sort of aromatic products produced by alkylation. However, there are some differences between methanol and formaldehyde as alkylating reagents; namely, the reactivity of formaldehyde to the alkylaromatics is more than that of methanol, and in the alkylation with formaldehyde, styrene was obtained in higher yield than ethylbenzene, while, with methanol, ethyl-

TABLE 1

ACTIVITY OF ALKALI CATION EXCHANGED ZEOLITES IN ALKYLATION WITH METHANOL[a]

Catalyst	% Exchanged	Yield[b] (mole %)					
		Ethylbenzene	Styrene	Xylene			Benzene
				o-	*m*-	*p*-	
LiY	81	0	0	3.1	1.0	1.1	Trace
SK-40	—	0	0	1.4	0.4	1.2	Trace
NaY[c]	—	Trace	Trace	0	0	0	0
KY	90	1.4	0.6	0	0	0	0
RbY	65	1.4	1.6	0	0	0	0
CsY	70	2.0	1.7	0	0	0	0
LiX	75	0	0	1.1	0.4	1.2	Trace
13X	—	0.1	0.5	0.36	0.05	0.19	Trace
NaX[c]	—	0.8	3.3	0	0	0	0
KX	90	5.1	1.9	0	0	0	0
RbX	70	6.8	4.2	0	0	0	0
CsX	77	Trace	1.2	0	0	0	0

[a] Conditions: $W/F = 25$ (g hr/mole); temp = 425°C; toluene/methanol = 6.

[b] The listed yield is taken at the highest alkylation activity on process time.

[c] NaY and NaX are prepared by the back-exchange of SK-40 and 13X with an aqueous solution of sodium acetate.

benzene was obtained in higher yield than styrene. These results may support the mechanism proposed by Sidorenko, *et al.* (*9*) in the alkylation with methanol on alkali zeolites; that is, in the first stage, methanol is converted to formaldehyde, and then reacts with toluene to produce styrene. However, it could be considered that ethyl-

TABLE 2

ACTIVITY OF ALKALI CATION EXCHANGED ZEOLITES IN ALKYLATION WITH FORMALDEHYDE[a]

Catalyst	% Exchanged	Yield[b] (mole %)					
		Ethylbenzene	Styrene	Xylene			Benzene
				o-	*m*-	*p*-	
LiY	81	0	0	2.4	3.4	4.9	1.3
SK-40	—	0	0	1.4	1.5	2.5	0.5
NaY[c]	—	Trace	Trace	0	0	0	0
KY	90	0.9	1.5	0	0	0	0
RbY	65	1.5	2.0	0	0	0	0
CsY	70	1.4	2.7	0	0	0	0
LiX	75	Trace	0	3.5	0.9	1.2	0.2
13X	—	1.3	0.6	0.2	0.2	0.5	Trace
NaX[c]	—	1.5	0.8	0	0	0	0
KX	90	3.4	6.3	0	0	0	0
RbX	70	2.6	10.3	0	0	0	0
CsX	77	1.2	6.3	0	0	0	0

[a] Conditions: $W/F = 25$ (g hr/mole); temp = 425°C; toluene/formaldehyde = 6; formaldehyde concn = 43 (wt %).

[b] The listed yield is taken at the highest alkylation activity on process time.

[c] NaY and NaX are prepared by the back-exchange of SK-40 and 13X with an aqueous solution of sodium acetate.

benzene was produced not only by hydrogenation of styrene but also by direct dehydrocondensation of the methyl group of toluene with methanol, when the ethylbenzene/styrene ratios with these two different reagents, i.e., methanol and formaldehyde, are taken into consideration, even though the hydrogen produced by dehydrogenation of methanol is used in hydrogenation of styrene.

Concerning the catalyst activity as a function of the percentage of ion exchange, Table 3 shows the results of alkylation of toluene with formaldehyde on potassium ion X zeolites exchanged to different extents. The yield of total C_8 aromatics increased with the percentage of ion exchange. However, beyond about 60% it does not increase markedly with the percentage exchange. Thus, it is concluded that in the formation of styrene and ethylbenzene, the catalyst activity has a tendency to be greater for the X type zeolites than for the corresponding Y type zeolites, and also depends on the basicity of alkali metal element; that is, Na < K < Rb < Cs. However, CsX has a lower activity for this alkylation, because of a partial destruction of its crystallinity.

The results of the alkylation of other aromatics with methanol and of toluene with ethylene on RbX are shown in Table 4. It was found that the alkylation of the side chain of toluene with ethylene proceeded over RbX, and also that the alkylating reagent was attached to the α-carbon of the side chain of the aromatics, because cumene and α-methylstyrene were selectively formed by the alkylation of ethylbenzene with methanol. Similar phenomena were observed in the alkylation of aromatics with olefins on basic catalysts (*12*) and in the radically proceeding alkylation at a high temperature (*13*). However, it could not be considered that such a high selectivity of product distribution could be obtained in the radical reaction.

Effects of acidic and basic reagent. Hydrogen chloride as an acidic reagent or aniline as a basic reagent was added to the reaction system, and their effects are summarized in Table 5. The addition of hydrogen chloride promoted the benzene ring alkylation of toluene and thus increased xylene yield, as in the case of LiY catalyst. Especially in the case of KY, RbY and CsY catalysts, on which only styrene and ethylbenzene were produced as shown in Table 2, were xylenes selectively formed under the same reaction conditions. On the other hand, aniline poisoned the formation of xylenes on LiY, but promoted that of styrene and ethylbenzene on KX and RbX. These results suggested that xylene formation, i.e., the alkylation of the benzene ring of toluene, is due to the catalyst acidity, and the formation of styrene and ethylbenzene, i.e., the alkylation of the side chain of toluene, is attributed to the catalyst basicity.

Catalyst acidity and basicity of alkali exchanged zeolites. Using the method of

TABLE 3
EFFECT OF PERCENTAGE EXCHANGED WITH POTASSIUM ION IN ALKYLATION WITH FORMALDEHYDE[a]

	Yield[b] (mole %)			
% Exchanged	Ethylbenzene	Styrene	Xylenes	Total C_8 aromatics
0 (13X)	1.3	0.6	0.9	2.8
47	3.4	5.1	0	8.5
62	3.5	5.9	0	9.4
69	3.4	6.1	0	9.5
81	3.5	6.1	0	9.6
90	3.4	6.3	0	9.7

[a] Conditions: $W/F = 25$ (g hr/mole), temp = 425°C, toluene/formaldehyde = 6, formaldehyde concn = 43 (wt %). Catalyst: KX.

[b] The listed yield is taken at the highest alkylation activity on process time.

TABLE 4

ALKYLATION OF AROMATICS WITH METHANOL AND ETHYLENE[a]

Aromatics (A)	Alkylating reagent (B)	(A)/(B)	Yield[b] (mole %)	
			o-Ethyltoluene	*o*-Methylstyrene
o-Xylene	Methanol	3/1	6.5	3.0
			m-Ethyltoluene	*m*-Methylstyrene
m-Xylene	Methanol	3/1	10.0	3.3
			p-Ethyltoluene	*p*-Methylstyrene
p-Xylene	Methanol	3/1	6.4	1.5
			Cumene	α-Methylstyrene
Ethylbenzene	Methanol	3/1	0.8	0.6
			n-Propylbenzene[c]	
Toluene	Ethylene	1/3	0.5	

[a] Conditions: $W/F = 50$ (g hr/mole); temp = 425°C. Catalyst: RbX.

[b] The listed yield is taken at the highest alkylation activity on process time.

[c] The yield of *n*-propyltoluene is calculated on the basis of fed toluene.

ir spectra measurement of pyridine adsorbed on zeolite, we observed the absorption band of pyridinium ion on the Brønsted acid site and of the coordinate bond between pyridine and Lewis acid site of LiY, LiX, SK-40 and 13X. But no acid site was observed on Na, K, Rb and Cs zeolites. Recently, Ward (*14*) has reported that neither the Brønsted acid site nor the Lewis acid site was observed on the alkali cation exchanged zeolites by the ir technique of pyridine adsorption. Watanabe and Habgood (*15*), however, have noticed the acidic hydroxyl group on LiY zeolite. The acidity of 13X and SK-40 is due to the impurities of multivalent cations (as mentioned above).

A linear relation between the yield of xylenes and the relative total acidity (Table 6), calculated using a conversion factor of 1.54 for the interconversion of Lewis to Brønsted sites (*16*), is shown

TABLE 5

EFFECT OF THE ADDITION OF ACIDIC AND BASIC REAGENTS[a]

Catalyst	Reagent	Yield[b] (mole %) Ethylbenzene	Styrene	Xylenes	Benzene
LiY	Hydrogen chloride	0	0	34.4	7.1
KY	Hydrogen chloride	0	0	9.5	1.0
RbY	Hydrogen chloride	0	0	8.7	Trace
CsY	Hydrogen chloride	0	0	6.6	Trace
LiY	Aniline (1 mole %)	0	0	Trace	0
KX	Aniline (1 mole %)	5.5	2.5	0	0
RbX	Aniline (1 mole %)	7.3	5.8	0	0

[a] Conditions: $W/F = 25$ (g hr/mole), temp = 425°C, toluene/methanol = 6.

[b] The listed yield is taken at the highest alkylation activity on process time.

TABLE 6
ABSORBANCE[a] OF PYRIDINE RETAINED BY ZEOLITES AND RELATIVE CATALYST ACIDITY[b]

Catalyst	Absorbance 1545 cm^{-1} (Bpy)	 1455 cm^{-1} (Lpy)	Relative total acidity (g^{-1})
LiY	0.018	0.028	3.05
SK-40	0.010	0.019	1.95
LiX	0.005	0.020	1.80
13X	0	0.004	0.30

[a] The value is obtained after successive treatments of the disk, and Brønsted pyridine at 1545 cm^{-1} and Lewis pyridine at 1455 cm^{-1} are calculated on the same scale per 20 mg catalyst.

[b] Relative total acidity is calculated using a conversion factor of 1.54 for the interconversion of Lewis to Brønsted sites.

in Fig. 11. This result supports the idea that the formation of xylenes depends on the catalyst acidity.

There is no ir measurement applicable for catalyst basicity. Hence an indicator such as cresol red (pH range 7.2–8.8) and thymolphthalein (pH range 9.3–10.5) was used to detect the basicity. KX and RbX showed the color of the basic form in the case of both indicators, while LiX did not. These results support the idea that the formation of styrene and ethylbenzene by the side-chain alkylation is due to the catalyst basicity. However, as these catalysts have only small amounts of base (<0.01 mEq/g), these basicities could not be measured exactly by the titration method using benzoic acid and cresol red.

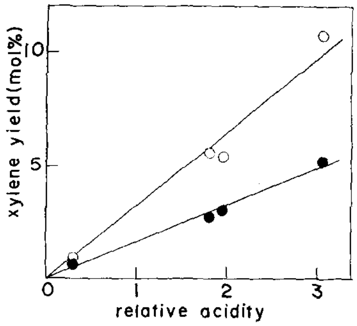

FIG. 11. Relation between xylene yield and relative acidity of catalyst. Conditions: $W/F = 25$ (g hr/mole), temp = 425°C, toluene/methanol or formaldehyde = 6, formaldehyde concn = 43 (wt %). (●) alkylation with methanol; (○) alkylation with formaldehyde.

CONCLUSION

1. Alkylation of toluene with methanol and with formaldehyde is promoted on alkali cation exchanged zeolites at a relatively high reaction temperature (>350°C). Xylenes and a mixture of styrene and ethylbenzene are selectively formed on Li zeolites and Na, K, Rb and Cs zeolites, respectively.
2. As alkylation reagents, methanol and formaldehyde have a similar tendency toward selective alkylation of toluene. Formaldehyde is more reactive than methanol in this alkylation.
3. It is suggested that the benzene ring alkylation of toluene depends on the catalyst acidity, on the basis of the catalyst poisoning with aniline and the linear relation between yield of xylenes and relative catalyst acidity. On the other hand, in consequence of the catalyst poisoning with hydrogen chloride and the detection of basic properties in KX and RbX, it is suggested that the side-chain alkylation of toluene depends on the catalyst basicity.

REFERENCES

1. GALICH, P. N., GOLUBCHENKO, I. T., GUTYRYA, V. S., IL'IN, V. G., AND NEIMARK, I. E., *Ukr. Khim. Zh.* **31**, 1117 (1965); *Chem. Abstr.* **64**, 12571 (1966).
2. BRYANT, D. E., AND KRANICH, W. L., *J. Catal.* **8**, 8 (1967).
3. KAWAKAMI, S., TAKANASHI, S., AND FUJII, S., *Kogyo Kagaku Zasshi* **74**, 889 (1971).
4. GALICH, P. N., *et al., Dokl. Akad. Nauk SSSR* **161**, 627 (1965); Venuto, P. B., and Landis, P. S., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, eds.), Vol. 18, p. 331. Academic Press, New York, 1968.
5. VENUTO, P. B., AND LANDIS, P. S., *in* "Advances in Catalysis and Related Subjects" (D. D. Eley, H. Pines, and P. B. Weisz, eds.), Vol. 18, p. 355. Academic Press, New York, 1968.
6. DIMITROV, C., AND LEACH, H. F., *J. Catal.* **14**, 336 (1969).

7. Yashima, T., Ahmad, H., Yamazaki, K., Katsuta, M., and Hara, N., *J. Catal.* **16**, 273 (1970).
8. Yashima, T., Yamazaki, K., Ahmad, H., Katsuta, M., and Hara, N., *J. Catal.* **17**, 151 (1970).
9. Sidorenko, Y. N., Galich, P. N., Gutyrya, V. S., Il'in, V. G., and Neimark, I. E., *Dokl. Akad. Nauk SSSR* **173**, 132 (1967).
10. Walker, J. F., *in* "Formaldehyde" p. 486. Reinhold, New York, 1964.
11. Lombardo, E. A., Sill, G. A., and Hall, W. K., "2nd International Conference on Molecular Sieve Zeolites, Worcester, 1970," prepr. p. 258. Amer. Chem. Soc., Washington, DC, 1970.
12. Voltz, S. E., *J. Org. Chem.* **22**, 48 (1957).
13. Pines, H., and Arrigo, J. T., *J. Amer. Chem. Soc.* **79**, 4958 (1957).
14. Ward, J. W., *J. Catal.* **10**, 34 (1968); **14**, 365 (1969).
15. Watanabe, Y., and Habgood, H. W., *J. Phys. Chem.* **72**, 3066 (1968).
16. Lefrancois, M., and Malbois, G., *J. Catal.* **20**, 350 (1971).